

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
26 April 2001 (26.04.2001)

PCT

(10) International Publication Number  
**WO 01/29096 A1**

- (51) International Patent Classification<sup>7</sup>: C08F 10/00, 4/645 (74) Agents: RUNYAN, Charles, E. et al.; ExxonMobil Chemical Company, P.O. Box 2149, Baytown, TX 77522-2149 (US).
- (21) International Application Number: PCT/US00/29197
- (22) International Filing Date: 23 October 2000 (23.10.2000) (81) Designated States (*national*): BR, CA, CN, JP, KR, MX, SG.
- (25) Filing Language: English (84) Designated States (*regional*): European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).
- (26) Publication Language: English
- (30) Priority Data:  
09/422,533 21 October 1999 (21.10.1999) US Published:  
— With international search report.  
— Before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments.
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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.



WO 01/29096 A1

(54) Title: HIGH ACTIVITY CARBENIUM-ACTIVATED POLYMERIZATION CATALYSTS

(57) Abstract: This application discloses triphenyl carbenium NCA's as catalyst activators for a class of asymmetrically bridged hafnocene catalyst precursors. These catalyst precursors are activated into olefin polymerization catalysts and are suitable for gas, solution, and slurry-phase polymerization reactions. The disclosed bridge is methylenyl- or silanylenyl-based and is optionally, alkyl or aryl substituted. The catalytic activity of the disclosed hafnocene catalyst precursors is substantially enhanced over identical catalysts that are activated with other activators.

# 1 HIGH ACTIVITY CARBENIUM-ACTIVATED POLYMERIZATION 2 CATALYSTS

**3 INVENTORS: Donna Crowther and Bernard Foley**

## 4 RELATED APPLICATIONS

5           This application is a CIP of US application Ser. No. 09/422,533,  
6   filed 21-October-1999 and that claimed the benefit of US prov. Application No.  
7   60/105,329, filed 23-October-1998.

## 9 TECHNICAL FIELD

10                    This invention relates to olefin copolymerization processes using  
11   substituted hafnocene catalyst compounds with noncoordinating anions.

## 13 BACKGROUND ART

Olefin polymers comprising ethylene and at least one or more  $\alpha$ -olefin and optionally one or more diolefin make up a large segment of polyolefin polymers and will be addressed as "ethylene copolymers" herein. Such polymers range from crystalline polyethylene copolymers to largely amorphous elastomers, with a new area of semi-crystalline "plastomers" in between. In particular, ethylene copolymer plastomers are now a well established class of industrial polymers having a variety of uses associated with their unique properties, such as elastomeric properties and their thermo-oxidative stability. Uses of the plastomers include general thermoplastic olefins, films, wire and cable coatings, polymer modification (by inclusion in blends with other polyolefins), injection molding, foams, footwear, sheeting, functionalized polymers (such as by free-radical graft addition of polar monomers) and components in adhesive and sealant compounds.

26 Commercially prepared ethylene copolymers have been traditionally  
27 been made via Ziegler-Natta polymerization with catalyst systems largely based on  
28 vanadium or titanium. Newer metallocene catalyst compounds have received

1 attention due to their ease of larger monomer incorporation and potential increases  
2 in polymerization activities. U.S. patent 5,324,800 describes metallocenes having  
3 substituted and unsubstituted cyclopentadienyl ligands which are suitable for  
4 producing high molecular weight olefin polymers, including linear, low density  
5 copolymers of ethylene with minor amounts of  $\alpha$ -olefin.

6 Additionally, polypropylene is an important industrial polymer. To  
7 the extent that catalysts for these polymerizations can be improved, their use  
8 provides economic benefit.

9 Noncoordinating anions useful as catalyst components with such  
10 metallocenes are known. The term "noncoordinating anion" is now accepted  
11 terminology in the field of olefin polymerization, both by coordination or insertion  
12 polymerization and carbocationic polymerization. The noncoordinating anions  
13 function as electronic stabilizing cocatalysts, or counterions, for cationic  
14 metallocenes which are active for olefin polymerization. The term  
15 "noncoordinating anion" as used here and in the references applies both to  
16 noncoordinating anions and weakly coordinating anions that are not so strongly  
17 coordinated to the cationic complex as so to be labile to replacement by  
18 olefinically or acetylenically unsaturated monomers at the insertion site. U.S.  
19 patent 5,198,401 describes a preferred noncoordinating anion  
20 tetra(perfluorophenyl) boron,  $[B(pfp)_4]^-$  or  $[B(C_6F_5)_4]^-$ , wherein the perfluorinated  
21 phenyl ligands on the boron makes the counterion labile and stable to potential  
22 adverse reactions with the metal cation complexes.

23  
24 The utility of metallocene-based ionic catalysts in high temperature  
25 olefin polymerization is described in U.S. patents 5,408,017 and 5,767,208, EP 0  
26 612 768, and WO 96/33227. Each addresses suitable metallocene catalysts for  
27 high temperature processes for olefin copolymerization. High molecular weight  
28 ethylene/ $\alpha$ -olefin copolymers is an objective of EP 0 612 768 and is addressed  
29 with catalyst systems based on bis(cyclopentadienyl/indenyl/fluorenyl) hafnocenes  
30 which are combined with an alkyl aluminum compound and an ionizing ionic  
31 compound providing a non-coordinating anion.

Improved catalyst systems for olefin polymerization are industrial useful.

#### BRIEF SUMMARY

The invention thus addresses specifically substituted, bridged hafnocene catalyst complexes activated with cocatalysts in which specific choices of catalyst and activator lead to unexpectedly high catalysis activities such that olefin copolymers and copolymers can be prepared at surprisingly high production rates. More specifically, the invention relates to catalysts for polymerizing olefins under supercritical or solution polymerization conditions at a reaction temperature at, or above, 60 °C to 225 °C, or below. Specific monomers useful in the invention include ethylene and/or propylene and one or more comonomers capable of insertion polymerization with a hafnocene catalyst complex derived from A) a biscyclopentadienyl hafnium organometallic compound having i) at least one unsubstituted cyclopentadienyl ligand or aromatic fused-ring substituted cyclopentadienyl ligand not having additional substituents on said ligand, ii) one substituted or unsubstituted, aromatic fused-ring substituted cyclopentadienyl ligand, and iii) a covalent bridge connecting the two cyclopentadienyl ligands where the bridge has a single carbon or silicon atom plus additional moieties that complete carbon or silicon's valence; and B) an activating cocatalyst, preferably a precursor ionic compound comprising a halogenated tetraaryl-substituted Group 13 anion and a carbenium cation.

#### DEFINITIONS

Carbenium cations are cations in which carbon has a formal valence of 3 leaving it with a +1 charge. Such a species is highly Lewis acidic and is a useful metallocene activator. Isoelectronic or isostructural cations in which the carbon is replaced with for example Si are also useful.

Cyclopentadienyl ligands: Cyclopentadienyl ligands are those ligands that have a cyclopentadiene anion core. These can be unsubstituted or

1 substituted with hydrocarbyl groups as defined below. They can be part of fused-  
2 ring systems such as indenyl and fluorenyl. Similarly the use of hetero-atom  
3 containing cyclopentadienyl rings or fused rings, where a non-carbon Group 14, 15  
4 or 16 atom replaces one of the ring carbons in the cyclopentadienyl ring or in a  
5 ring fused with the cyclopentadienyl ring is within the scope of cyclopentadienyl.  
6 The important component of a cyclopentadienyl ligand for this disclosure is that  
7 the ligand retain the aromatic, substantially planar, five-membered ring of the  
8 cyclopentadienide anion. The terms "indenyl" and "fluorenyl" ligands are  
9 therefore within the scope of cyclopentadienyl. When this disclosure wishes to  
10 refer to cyclopentadienide itself, it uses cyclopentadienide or cyclopentadiene  
11 anion. See, for example, the teachings of WO 98/37106, having common priority  
12 with U.S. Ser. No. 08/999,214, filed 12/29/97, and WO 98/41530, having common  
13 priority with U.S. Ser. No. 09/042,378, filed 3/13/98, incorporated by reference for  
14 purposes of U.S. patent practice.

15 Cyclopentadienyl substitutions R and R', typically include one or  
16 more C<sub>1</sub> to C<sub>30</sub> hydrocarbon or hydrocarbylsilyl groups selected from linear,  
17 branched, cyclic, aliphatic, aromatic or combined structure groups, including  
18 fused-ring or pendant configurations. Examples include methyl, isopropyl, n-  
19 propyl, n-butyl, isobutyl, tertiary butyl, neopentyl, phenyl, n-hexyl, cyclohexyl,  
20 and benzyl.

21 T is a bridge with two aryl groups, each substituted with a C<sub>1</sub> - C<sub>20</sub>  
22 hydrocarbyl or hydrocarbylsilyl group at least one of which is a linear C<sub>3</sub> or greater  
23 substituent. The bridge substituents preferably comprise C<sub>1</sub>-C<sub>20</sub> linear or branched  
24 alkyl, or C<sub>1</sub>-C<sub>20</sub> substituted-silyl, substituted phenyl groups, the alkyl or  
25 substituted-silyl substituents located in the para- or meta-positions of the aryl  
26 groups, preferably wherein at least one of said alkyl substituents is a C<sub>3</sub> or higher  
27 linear n-alkyl substituent, preferably C<sub>4</sub> or higher. Specific examples include  
28 methyl, ethyl, n-propyl, n-butyl, sec-butyl, isobutyl, tert-butyl, n-pentyl, neopentyl,  
29 etc.

30 Q are hafnocene ligands that can be abstracted by the activator and  
31 are ligands that a olefin monomer can insert into as polymerization occurs. Q

1 substituents specifically include fluorinated aryl groups, preferably perfluorinated  
2 aryl groups, and include substituted Q groups having substituents additional to the  
3 fluorine substitution, such as fluorinated hydrocarbyl groups. Preferred fluorinated  
4 aryl groups include phenyl, biphenyl, naphthyl, and derivatives thereof. The  
5 disclosures of U.S. Patents 5,198,401, 5,296,433, 5,278,119, 5,447,895, 5,688,634,  
6 5,895,771, WO 93/02099, WO 97/29845, WO 99/43717, WO 99/42467 and  
7 copending U.S. Application Serial Number 09/261,627, filed 3 March 1999, and  
8 its equivalent WO 99/45042 are particularly instructive as to suitable Q  
9 substituents and are incorporated by reference for purposes of U.S. patent practice.

10           Hydrocarbyl: For the purposes of this application the term  
11 "hydrocarbon" or "hydrocarbyl" is meant to include those compounds or groups  
12 that have essentially hydrocarbon characteristics but optionally contain not more  
13 than about 10 mol.% non-carbon atoms, such as boron, silicon, oxygen, nitrogen,  
14 sulfur and phosphorous. "Hydrocarbylsilyl" is exemplified by, but not limited to,  
15 dialkyl- and trialkylsilyls.

16           Alkyl is a radical based on an aliphatic hydrocarbon. This backbone  
17 can be substituted by any number of other alkyl or aryl substituents as is known in  
18 the art.

19           Aryl is a radical based on an aromatic hydrocarbon. This backbone  
20 can be substituted by any number of other aryl or alkyl substituents as is known in  
21 the art.

22           NCA is a non-coordinating ion. This term encompasses anions that  
23 are coordinating but only weakly so. The key is that incoming olefin monomer is  
24 capable of replacing NCA during a polymerization process.

25

## 26 DETAILED DESCRIPTION

27           The bridged hafnium compounds of the invention include those  
28 having a single substituted carbon or silicon atom bridging two cyclopentadienyl-  
29 containing (Cp) ligands of the hafnium metal centers. The Cp ligands are either  
30 substituted or unsubstituted, preferably substituted. The bridge is either

1 methyleneyl or silylenyl-based and is substituted or unsubstituted, preferably  
2 substituted.

3                   Specific bridged hafnium catalysts include those derived from: (1)  
4 indenyl-based complexes such as the isomers, or mixtures, of (para-n-  
5 butylphenyl)(para-t-butylphenyl)methylene (fluorenyl) (indenyl) hafnium  
6 dimethyl, (para-n-propylphenyl)(para-methylphenyl)methylene (fluorenyl)  
7 (indenyl) hafnium dimethyl, di(para-n-butylphenyl)methylene (2,7-di tertbutyl  
8 fluorenyl) (indenyl) hafnium dimethyl, (para-n-butylphenyl)(para-t-  
9 butylphenyl)methylene (2,7-di tertbutyl fluorenyl) (indenyl) hafnium dimethyl,  
10 (para-n-butylphenyl)(para-t-butylphenyl)methylene (2,7-dimethyl  
11 fluorenyl)(indenyl) hafnium dibenzyl and di(para-n-butylphenyl) methylene  
12 (fluorenyl) (indenyl) hafnium dimethyl; and, (2) fluorenyl-based complexes such  
13 as (para-n-propylphenyl)(para-i-propylphenyl)silyl (fluorenyl) (fluorenyl) hafnium  
14 di-t-butyl, di(para-n-propylphenyl)methylene (2,7-di-tert-butyl-5-methylfluorenyl)  
15 (fluorenyl) hafnium dimethyl; and (3) cyclopentadienyl-based complexes such as  
16 the isomers, or mixtures, of (para-n-propylphenyl)(para-i-propylphenyl)methylene  
17 (fluorenyl) (cyclopentadienyl) hafnium dimethyl, (para-n-butylphenyl)(para-t-  
18 butylphenyl)methylene (fluorenyl) (cyclopentadienyl) hafnium dimethyl, di(para-  
19 n-butylphenyl)methylene (2,7-di tertbutyl fluorenyl) (cyclopentadienyl) hafnium  
20 dimethyl, (para-n-butylphenyl)(para-t-butylphenyl)methylene (2,7-di tertbutyl  
21 fluorenyl) (cyclopentadienyl) hafnium dimethyl, and di(para-n-  
22 butylphenyl)methylene (2,7-dimethyl fluorenyl)(cyclopentadienyl) hafnium  
23 dimethyl or dibenzyl. It has been found that the substituted bridge-containing  
24 compounds, such as those asymmetric compounds listed above, are particularly  
25 useful in accordance with the invention.

26  
27                   The invention activating cocatalyst, precursor ionizing compounds  
28 comprise Group 13 element complexes having at least two halogenated aromatic  
29 ligands such as the halogenated tetraphenyl boron and aluminum compounds  
30 exemplified in the identified prior art.

1                   Those anions with mixed ligands are also suitable.  
2   Tris(perfluorophenyl) (perfluoronaphthyl) borate is an illustrative complex. Thus,  
3   generically speaking, the Group 13 complexes useful in accordance with the  
4   invention will typically conform to the following formula:

5



7  
8   where, M is a Group 13 element, A is a nonhindering ligand as described above,  
9   C is a hindering ligand, one having bulky substituents on the closest aryl ring  
10   bonded to the metal/metalloid center other than those described as suitable above,  
11   and n = 0, 1, or 2. See also copending application U.S. serial number 60/087447,  
12   filed 1 June 1998, and its equivalent WO 99/45042, the teachings of which are  
13   referred to and incorporated by reference for purposes of U.S. patent practice.

14

15                   For both fused aromatic rings and aromatic ring assemblies, the  
16   halogenation is highly preferred so as to allow for increased charge dispersion that  
17   contributes along with steric bulk as independent features decreasing the likelihood  
18   of ligand abstraction by the strongly Lewis acidic metallocene cation formed in the  
19   catalyst activation. Additionally, halogenation inhibits reaction of the hafnium  
20   cation with any remaining carbon-hydrogen bonds of the aromatic rings, and  
21   perhalogenation precludes such potential undesirable reactions. Thus it is  
22   preferred that at least one third of hydrogen atoms on carbon atoms of the aryl  
23   ligands can be replaced by halogen atoms, and more preferred that the aryl ligands  
24   be perhalogenated. Fluorine is the most preferred halogen, perfluorinated aryl  
25   ligands are most preferred.

26

27                   Means of preparing ionic catalyst systems comprising catalytically  
28   active cations of the hafnium compounds and suitable noncoordinating anions are  
29   conventionally known, see for example U.S. patent 5,198,401, WO 92/00333, WO  
30   97/22639, and EP 0 612 768. Typically the methods comprise obtaining from  
31   commercial sources or synthesizing the selected transition metal compounds

1 comprising an abstractable ligand, e.g., hydride, halide, alkyl, alkenyl or hydro-  
2 carbyl-silyl group, and contacting them with a noncoordinating anion source or  
3 suitable precursor compounds in a suitable solvent. The anion precursor  
4 compound abstracts a monoanionic ligand (or one monoanionic bond of bidentate  
5 alkenyl ligands) that completes the valency requirements of the preferred hafnium  
6 metallocene compounds. The abstraction leaves the hafnocenes in an essentially  
7 cationic state which is counterbalanced by the stable, compatible and bulky,  
8 noncoordinating anions according to the invention. Each of the documents of this  
9 paragraph are incorporated by reference for purposes of U.S. patent practice.

10  
11           The noncoordinating anions are preferably introduced into the  
12 catalyst preparation step as ionic compounds having an essentially cationic  
13 complex which abstracts a non-cyclopentadienyl, labile ligand of the transition  
14 metal compounds which upon abstraction of the non-cyclopentadienyl ligand,  
15 leave as a by-product the noncoordinating anion portion. Hafnium compounds  
16 having labile hydride, alkyl, or silyl ligands on the metal center are highly  
17 preferred for the ionic catalyst systems of this invention since known in situ  
18 alkylation processes may result in competing reactions and interactions that tend to  
19 interfere with the overall polymerization efficiency under high temperature  
20 conditions in accordance with the preferred process embodiments of the invention.

21  
22           Suitable cations for precursor compounds capable of providing the  
23 noncoordinating anions of the invention cocatalysts include those known in the art,  
24 in which the cation is a carbenium or an analog of carbenium. Such include the  
25 carbenium, oxonium or sulfonium cations of US patent 5,387,568.

26           Examples of suitable anionic precursors include those comprising a  
27 stable carbenium ion, and a compatible non-coordinating anion. These include  
28 tropillium tetrakis(perfluoronaphthyl) or tetrakis(perfluoro-4-biphenyl) borate,  
29 triphenylmethylium tetrakis(perfluoronaphthyl) or tetrakis(perfluoro-4-biphenyl)  
30 borate, benzene (diazonium) tetrakis(perfluoronaphthyl) or tetrakis(perfluoro-4-  
31 biphenyl) borate, tropillium tetrakis(perfluoronaphthyl) or tetrakis(perfluoro-4-  
32 biphenyl) borate, triphenylmethylium tetrakis(perfluoronaphthyl) or

1 tetrakis(perfluoro-4-biphenyl)borate, benzene (diazonium)  
2 tetrakis(perfluoronaphthyl) or tetrakis(perfluoro-4-biphenyl) borate, tropillium  
3 tetrakis(perfluoronaphthyl) or tetrakis(perfluoro-4-biphenyl)borate,  
4 triphenylmethylium tetrakis(perfluoronaphthyl) or tetrakis(perfluoro-4-  
5 biphenyl)borate, benzene (diazonium) tetrakis(perfluoronaphthyl) or  
6 tetrakis(perfluoro-4-biphenyl)borate. The essentially structurally equivalent  
7 silylium borate or aluminate salts are similarly suitable.

8               The term "scavenger" as used in this application is used in its art-  
9 recognized sense of being sufficiently Lewis acidic to coordinate with polar  
10 contaminants and impurities adventitiously occurring in the polymerization  
11 feedstreams or reaction medium. Such impurities can be inadvertently introduced  
12 with any of the polymerization reaction components, particularly with solvent,  
13 monomer and catalyst feed, and adversely affect catalyst activity and stability. In  
14 particular, for processes utilizing recycle streams of unconverted monomer for  
15 reprocessing, the necessity to use polar compounds as catalyst deactivators, or  
16 "killers", such as water or lower alcohols, effectively necessitates the use of  
17 scavengers, as does the natural occurrence of polar impurities in monomer  
18 feedstreams. It can result in decreasing or even elimination of catalytic activity,  
19 particularly when a metallocene cation-noncoordinating anion pair is the catalyst  
20 system. The polar impurities, or catalyst poisons include water, oxygen, metal  
21 impurities, etc. Preferably steps are taken before provision of such into the  
22 reaction vessel, for example by chemical treatment or careful separation  
23 techniques after or during the synthesis or preparation of the various components,  
24 but some minor amounts of scavenging compound will still normally be required  
25 in the polymerization process itself.

26               Typically the scavenging compound will be an organometallic  
27 compound such as the Group-13 organometallic compounds of US patent  
28 5,241,025, EP-A-0 426 638 and those of U.S. patent 5,767,208. Exemplary  
29 compounds include triethyl aluminum, triethyl borane, tri-isobutyl aluminum,  
30 methylalumoxane, isobutyl aluminumoxane, tri-n-hexyl aluminum and tri-n-octyl  
31 aluminum, those having bulky substituents covalently bound to the metal or

1 metalloïd center being preferred to minimize adverse interaction with the active  
2 catalyst. Addition of excess scavenger causes lower productivity, molecular  
3 weight and comonomer incorporation. The aluminum to hafnium molar ratios  
4 (Al:Hf) should accordingly be less than about 100: 1, preferably less than about  
5 75:1, more preferably less than about 50 :1, and most preferably less than about  
6 30:1. Molar ratios of less than 20:1 and less than 15:1 have been observed to be  
7 sufficient for the continuous processes described in this application.

8  
9           The preferred scavenger is a long chain, linear tri-alkyl aluminum  
10 compound, and that longer chains are preferred over shorter chains. See WO  
11 97/22635 and U.S. patent 5,767,208 for further discussion, this document is  
12 incorporated by reference for purposes of U.S. patent practice. Non-limiting  
13 examples of effective long chain, linear tri-alkyl ligand-containing scavengers  
14 include those comprised in the group defined by the formula  $M'R'R''R'''$ , where  $M'$   
15 is Al, and each of the R groups independently is a  $C_4$  or higher linear, branched or  
16 cyclic alkyl group, preferably  $C_6$  or higher, most preferably  $C_8$  or higher. The long  
17 chain, linear alkyl aluminums where each alkyl substituent was of a length of  $C_8$  or  
18 higher, preferably  $C_9$  and higher were observed to exhibit optimal performance,  
19 that defined as having the least deleterious effect when used at a level in excess of  
20 the optimum level as described in the following paragraph. Specifically included  
21 are: tri-n-octyl aluminum, tri-n-decyl aluminum, tri-n-dodecyl aluminum, tri-n-  
22 hexadecyl aluminum, and the higher carbon number equivalents, e.g.,  $(C_{20})_3Al$ ,  
23 including those with mixed ligation, and mixed scavenger compounds as well.  
24 The hydrolyzed derivatives of these alkyl-ligand containing organoaluminum  
25 compounds will additionally be suitable. Additionally, it will be apparent that  
26 those scavenging compounds comprising both long-chain, linear and bulky ligands  
27 or mixed linear ligands, each ligand as described above, will also be suitable, but  
28 perhaps less desirable due to more involved or expensive syntheses.

29  
30           A preferred polymerization process is that designed or  
31 conducted such that the cocatalyst components, that is the transition metal  
32 compounds and the anion precursor compounds, are maintained separately until

1 just prior to or during polymerization use in the chosen reactor or reactors. An  
2 example is the use of dual injection of each catalyst component directly into the  
3 reactor or the use of T- or multi-joint mixing chambers just prior to injection into  
4 the reactor. Additional optimization can be achieved when the scavenger  
5 compound is introduced into the reactor independently of the catalyst system or  
6 compounds, preferably after the activation of the hafnocenes with the anion  
7 precursor cocatalysts.

8  
9           The process of the invention is applicable to high pressure  
10 homogeneous polymerization, preferably employing less than 30 wt% of solvent,  
11 which is substantially adiabatic and where the heat of polymerization is  
12 accommodated by a rise in temperature of the reactor contents instead of internal  
13 or external cooling. In this case, the contents consist principally of unreacted  
14 monomer. Such process may be performed, under a single or dual phase  
15 homogeneous conditions at pressures from 250 to 3000 bar, preferably from 500 to  
16 2500 bar, with or without unreactive diluents or solvents at temperatures generally  
17 above the melting point of the polymer being produced. Such processes are  
18 industrially known and may include the use of scavenger compounds and catalyst  
19 deactivation or killing steps, see for example U.S. patent 5,408,017, WO 95/07941,  
20 and WO 92/14766. Each of these documents and their U.S. counterparts are  
21 incorporated by reference for purposes of U.S. patent practice. Preferred catalyst  
22 deactivators, or killers, include high molecular weight, non-recyclable compounds,  
23 such as poly vinyl alcohol which exhibit the functional capacity to complex with  
24 the catalysts so as to deactivate them while not forming volatile polar by-products  
25 or residual unreacted compounds.

26  
27           The process of the invention is also especially applicable to  
28 homogeneous solution polymerization which is also substantially adiabatic, that is  
29 to say the heat of polymerization is accommodated by a rise in temperature of the  
30 polymerization reactor contents, here principally solvent. This adiabatic process  
31 typically would have no internal cooling and suitably no external cooling. The  
32 reactor outlet stream removes the heat of polymerization from the reactor. The

1 productivity of such adiabatic processes can be improved by cooling the inlet  
2 solvent and/or monomer stream(s) prior to introduction into the reactor to permit a  
3 greater polymerization exotherm. Thus the catalyst, cocatalyst and scavenger  
4 selections disclosed in this application can be advantageously practiced in a  
5 continuous, solution process operated at or above 140 °C, above 150 °C or above  
6 160 °C, up to about 225 °C. Most preferably the solution polymerization process  
7 for semi-crystalline polymers operated at a temperature from 140 °C - 220 °C.  
8 Typically this process is conducted in an inert hydrocarbon solvent, linear, cyclic  
9 or branched aliphatic, or aromatic, at a pressure of from 20 to 200 bar.

10           The  $\alpha$ -olefins suitable for use in the preparation of the ethylene  
11 copolymers, or for the polyethylene copolymers, are preferably C<sub>3</sub> to C<sub>20</sub>  $\alpha$ -olefins,  
12 but will include higher carbon number olefins such as polymerizable macromers  
13 having up to five hundred carbon atoms, or more. Illustrative non-limiting  
14 examples of such  $\alpha$ -olefins are one or more of propylene, 1-butene, 1-pentene, 1-  
15 hexene, 1-octene, and 1-decene. Included in the term olefins for the purposes of  
16 describing effectively copolymerized monomers are the constrained-ring cyclic  
17 monoolefins such as cyclobutene, cyclopentene, norbornene, alkyl-substituted  
18 norbornes, alkenyl-substituted norbornenes, and the higher carbon number cyclic  
19 olefins known in the art, see U.S. patent 5,635,573, incorporated herein by  
20 reference for purposes of U.S. patent practice, and known copolymerizable  
21 diolefins, e.g., 1,4-hexadiene, ethylidene-norbornene, and vinyl-norbornene. Vinyl  
22 aromatic monomers, e.g., styrene and alkyl-substituted styrene monomers are  
23 additionally suitable. The polyethylene copolymers can range from  
24 semicrystalline to substantially amorphous; and will typically have a substantially  
25 random arrangement of at least the ethylene and the olefin comonomers. As will  
26 also be apparent to those skilled in the art, the use of asymmetrically substituted  
27 hafnium compounds of the invention enable the preparation of syndiotactic  
28 polymers from prochiral olefins, e.g., like propylene. Processes for such will also  
29 benefit from the increased productivity and molecular weights described here for  
30 ethylene copolymers.

1                   The effective Group 8-15 element cocatalyst complexes of the  
2 invention are, in a preferable embodiment, derived from an ionic salt, comprising  
3 a 4-coordinate Group 10-14 element anionic complex, where  $A^-$  can be  
4 represented as:



6 where M is one or more Group 10-15 metalloid or metal, preferably boron or  
7 aluminum, and either each Q is ligand effective for providing electronic or steric  
8 effects rendering  $[(M')Q_1Q_2 \dots Q_n]^-$  suitable as a noncoordinating anion as that is  
9 understood in the art, or a sufficient number of Q are such that  $[(M')Q_1Q_2 \dots Q_n]^-$   
10 as a whole is an effective noncoordinating or weakly anion.

11 Additional suitable anions are known in the art and will be suitable  
12 for use with the metallocene catalysts of the invention. See U.S. Patent 5,483,014,  
13 weakly coordinating anions from borane, carborane, borate, carborate,  
14 metalloborane, or metallocarborane complexes are described and exemplified. See  
15 also, the review articles by S. H. Strauss, "The Search for Larger and More Weakly  
16 Coordinating Anions", *Chem. Rev.*, *93*, 927-942 (1993) and C. A. Red,  
17 "Carboranes: A New Class of Weakly Coordinating Anions for Strong  
18 Electrophiles, Oxidants and Superacids", *Acc. Chem. Res.*, *31*, 133 -139 (1998).

19 In particular embodiments one Q group, or ligand, of the anionic  
20 complex may also be bonded to a metal/metalloid oxide support or polymeric  
21 support. See, for example, U.S. Patents 5,427,991 and 5,939,347, each  
22 incorporated by reference for purposes of U.S. patent practice. Metal or metalloid  
23 oxide supports of the described bonding method for the invention include any  
24 metal/metalloid oxides, preferably those having surface hydroxyl groups  
25 exhibiting a pKa equal to or less than that observed for amorphous silica, i.e., pKa  
26 less than or equal to about 11. Accordingly, any of the conventionally known  
27 silica support materials that retain hydroxyl groups after dehydration treatment  
28 methods will be suitable in accordance with the invention. Because of availability,  
29 both of silica and silica containing metal oxide based supports, for example, silica-  
30 alumina, are preferred. Silica particles, gels, and glass beads are most typical.

1                   Polymeric supports are preferably hydroxyl-functional-group-  
2 containing polymeric substrates, but functional groups may be any of the primary  
3 alkyl amines, secondary alkyl amines, and others, where the groups are structurally  
4 incorporated in a polymeric chain and capable of a acid-base reaction with the  
5 Lewis acid such that a ligand filling one coordination site of the Group 13 element  
6 is protonated and replaced by the polymer incorporated functionality. See, for  
7 example, the functional group containing polymers of U.S. Patent 5,288,677, the  
8 functionalized polymers of U.S. Patents 5,427,991 and the descriptions in  
9 copending applications U.S. Serial No. 09/277,339, filed 26 March 1999, and its  
10 equivalent PCT/99US/06135, and U.S. Serial No. 09/092,752, filed 5 June 1998,  
11 and its equivalent WO 98/55518. All are incorporated by reference for purposes of  
12 U.S. patent practice.

13                   Other known methods for supporting catalyst systems comprising a  
14 noncoordinating anion cocatalyst will also be suitable as means for supporting the  
15 catalyst complexes of this invention. Thus, the catalyst complexes of the invention  
16 may also physically deposited on or affixed to a suitable support material. See, for  
17 example, the teachings of WO 91/09882, WO 93/11172, WO 96/35726 and U.S.  
18 Patents 4,463,135, and 5,610,115.

19 When using the above catalysts, the catalyst system will generally employ one or  
20 more scavenging agents to remove polar impurities from the reaction environment  
21 and to increase catalyst activity. Any polymerization-reaction components,  
22 particularly solvents, monomers, and catalyst feeds, can inadvertently introduce  
23 impurities and adversely affect catalyst activity and stability. Impurities decrease  
24 or even eliminate catalytic activity, particularly with ionizing-anion-activated  
25 catalyst systems. Polar impurities, or catalyst poisons, include water, oxygen,  
26 metal impurities, etc. Preferably, these impurities are removed from or reduced in  
27 the reaction components before their addition to the reaction vessel. Impurities  
28 can be removed by chemically treating the components or by impurity separation  
29 steps. Such treatment or separation can occur during or after synthesis of the  
30 components. In any case, the polymerization process will normally employ minor  
31 amounts of scavenging agent. Typically, these scavengers will be organometallic

1 such as the Group-13 compounds of U.S. patents 5,153,157, 5,241,025 and WO-A-  
2 91/09882, WO-A-94/03506, WO-A-93/14132, and that of WO 95/07941.  
3 Exemplary compounds include triethyl aluminum, triethyl borane, triisobutyl  
4 aluminum, methylalumoxane, and isobutyl alumoxane. Those compounds having  
5 bulky or C<sub>6</sub>-C<sub>20</sub> linear hydrocarbyl substituents covalently bound to the metal or  
6 metalloid center are preferred because they coordinate to the active catalyst more  
7 weakly. Examples include triethylaluminum, but more preferably, bulky  
8 compounds such as triisobutylaluminum, triisoprenylaluminum, and long-chain,  
9 linear-alkyl-substituted aluminum compounds, such as tri-n-hexylaluminum, tri-n-  
10 octylaluminum, or tri-n-dodecylaluminum. When alumoxane is used as activator,  
11 any excess over that needed to activate the catalyst can act as a scavenger and  
12 additional organometallic scavengers may be unnecessary. Alumoxanes also may  
13 be used as scavengers with other activators, e.g., methylalumoxane and triisobutyl-  
14 alumoxane with boron-based activators. The scavenger amount is limited to that  
15 amount effective to enhance activity (and with that amount necessary for  
16 activation when used in a dual role) since excess amounts may act as catalyst  
17 poisons.

18 This invention's catalyst system can polymerize those unsaturated monomers  
19 conventionally recognized as polymerizable using metallocenes. Typical  
20 conditions include solution, slurry, gas-phase, and high-pressure polymerization.  
21 The catalysts may be supported on inorganic oxide or polymeric supports and as  
22 such will be particularly useful in those operating modes employing fixed-bed,  
23 moving-bed, fluid-bed, slurry, or solution processes conducted in single, series, or  
24 parallel reactors. Invention cocatalysts may also function in catalyst pre-  
25 polymerization. WO 98/55518, incorporated by reference for purposes of U.S.  
26 patent practice, describes a preferred invention support method for gas-phase or  
27 slurry polymerization.

28           Alternative embodiments of this invention's olefin polymerization  
29 methods employ the catalyst system in liquid phase (solution, slurry, suspension,  
30 bulk phase, or combinations thereof), in high-pressure liquid or supercritical fluid  
31 phase, or in gas phase. These processes may also be employed in singular,

1 parallel, or series reactors. The liquid processes comprise contacting olefin  
2 monomers with the catalyst system described above in a suitable diluent or solvent  
3 and allowing those monomers to react long enough to produce the invention  
4 polymers. The term polymer encompasses both homo- and co-polymers. Both  
5 aliphatic and aromatic hydrocarbyl solvents are suitable; hexane is preferred. In  
6 bulk and slurry processes, the supported catalysts typically contacts a liquid  
7 monomer slurry. Gas-phase processes typically use a supported catalyst and  
8 follow any manner suitable for ethylene polymerization. Illustrative examples  
9 may be found in U.S. patents 4,543,399, 4,588,790, 5,028,670, 5,382,638,  
10 5352,749, 5,408,017, 5,436,304, 5,453,471, and 5,463,999, 5,767,208 and WO  
11 95/07942. Each is incorporated by reference for purposes of U.S. patent practice.  
12 The minimum polymerization reaction temperature is about 40°C. Preferably, the  
13 minimum reaction temperature is about 60°C. The temperature can go as high as  
14 about 250°C, but preferably does not exceed 220°C. The minimum reaction  
15 pressure is about 1 mm Hg, preferably about 0.1 bar, and most preferably 1.0 bar.  
16 The maximum pressure is less than or equal to about 2500 bar, preferably 1600 bar  
17 or lower, but most preferably 500 bar or less.  
18 Invention catalysts can produce several types of linear polyethylene including  
19 high- and ultra-high-molecular-weight polyethylenes, including both homo- and  
20 copolymers with other alpha-olefin monomers or alpha-olefinic or non-conjugated  
21 diolefins, e.g. C<sub>3</sub> - C<sub>20</sub> olefins, diolefins, or cyclic olefins. The polyethylenes are  
22 produced by adding ethylene, and optionally one or more other monomers, with  
23 invention activated catalysts that have been slurried with a solvent, such as hexane  
24 or toluene, to a reaction vessel under low pressure (typically < 50 bar), at a typical  
25 temperature of 40-250 °C. Cooling typically removes polymerization heat. Gas-  
26 phase polymerization can be conducted, for example, in a continuous fluid-bed,  
27 gas-phase reactor operated at a minimum of 2000 kPa and up to 3000 kPa. The  
28 minimum temperature is 60°C; the maximum temperature is 160°C. The gas-phase  
29 reaction uses hydrogen as a reaction modifier at a concentration of no less than 100  
30 PPM. The hydrogen gas concentration should not exceed 200 PPM. The reaction  
31 employs a C<sub>4</sub> - C<sub>8</sub> comonomer feedstream and a C<sub>2</sub> feedstream. The C<sub>4</sub> - C<sub>8</sub>

1 feedstream goes down to 0.5 mol%. It also may go up to 1.2 mol%. Finally, the  
2 C<sub>2</sub> feedstream has a minimum concentration of 25 mol%. Its maximum  
3 concentration is 35 mol%. See, U.S. patents 4,543,399, 4,588,790, 5,028,670 and  
4 5,405,922 and 5,462,999, which are incorporated by reference for purposes of U.S.  
5 patent practice.

6 High-molecular-weight, low-crystallinity, ethylene- $\alpha$ -olefin elastomers (including  
7 ethylene-cyclic-olefin and ethylene- $\alpha$ -olefin-diolefin elastomers) can be prepared  
8 using catalysts activated by this inventions activators under traditional solution  
9 polymerization processes or by introducing ethylene gas into invention catalyst  
10 slurries with  $\alpha$ -olefin, cyclic olefin, or either or both mixed with other  
11 polymerizable and non-polymerizable diluents. Typical ethylene pressures range  
12 from about 10 to about 1000 psig (69-6895 kPa) and the diluent temperature  
13 typically remains between about 40 and about 160 °C. The process can occur in  
14 one or more stirred tank reactors, operated individually, in series, or in parallel.  
15 See the general disclosure of U.S. patent 5,001,205 for general process conditions.  
16 See also, international application WO 96/33227 and WO 97/22639. All  
17 documents are incorporated by reference for purposes of US patent practice.

18 Besides those specifically described above other monomers may be polymerized  
19 using the invention's catalyst systems, for example, styrene, alkyl-substituted  
20 styrenes, isobutylene and other geminally disubstituted olefins, ethylidene  
21 norbornene, norbornadiene, dicyclopentadiene, and other olefinically-unsaturated  
22 monomers, including other cyclic olefins, such as cyclopentene, norbornene, alkyl-  
23 substituted norbornenes, and vinyl-group-containing, polar monomers capable of  
24 coordinating polymerization. See, for example, U.S. patents 5,635,573, 5,763,556,  
25 and WO 99/30822. Additionally,  $\alpha$ -olefin macromonomers of up to 1000 mer units  
26 or more may be copolymerized yielding branched olefin polymers. Additionally,  
27 oligomerization, dimerization, hydrogenation, olefin/carbon-monoxide  
28 copolymerization, hydroformulation, hydrosilation, hydroamination, and related  
29 catalytic reactions catalyzed by activated cation complexes can be activated with  
30 invention cocatalyst activators.

1 The invention activators can be used to activate catalysts as described above  
2 individually for coordination polymerization or can activate mixed catalysts for  
3 polymer blends. Adept monomers and catalyst selection yields polymer blends  
4 analogous to those using individual catalyst compositions. Polymers having  
5 increased MWD for improved processing and other traditional benefits available  
6 from polymers made with mixed catalyst systems can be achieved using invention  
7 cocatalysts.

8 Blended polymer formation can be achieved ex situ through  
9 mechanical blending or in situ through using mixed catalyst systems. It is  
10 generally believed that in situ blending provides a more homogeneous product and  
11 allows the blend to be produced in one step. In-situ blending with mixed catalyst  
12 systems involves combining more than one catalyst in the same reactor to  
13 simultaneously produce multiple, distinct polymer products. This method requires  
14 additional catalyst synthesis, and the various catalyst components must be matched  
15 for their activities, the polymer products they generate at specific conditions, and  
16 their response to changes in polymerization conditions. Invention cocatalyst  
17 activators can activate mixed catalyst systems.

18 Ethylene- $\alpha$ -olefin (including ethylene-cyclic olefin and ethylene- $\alpha$ -  
19 olefin-diolefin) elastomers of high molecular weight and low crystallinity can be  
20 prepared using the invention catalysts under traditional solution polymerization  
21 conditions or by introducing ethylene gas into a slurry of polymerization diluent  
22 and catalyst. The polymerization diluent contains  $\alpha$ -olefin monomers, cyclic  
23 olefin monomers, or their mixtures with other polymerizable and non-  
24 polymerizable monomers. In this case, polymerization reaction pressure varies, as  
25 well. The minimum pressure is 0.0013 bar; a pressure of at least 0.1 bar is more  
26 preferred. Most preferably, the reaction pressure is at least 1.0 bar. The maximum  
27 pressure is 2500 bar, with a pressure at most 1600 bar being preferred. The most  
28 preferred maximum pressure is 500 bar. Typical ethylene pressures will be  
29 between 10 and 1000 psig (69-6895 kPa) and the polymerization diluent  
30 temperature will typically be between -10 and 160°C. The process can use a  
31 stirred-tank reactor, or more than one reactor operated in series or parallel. See the

1 general disclosure of U.S. Patent 5,001,205, which is incorporated by reference for  
2 its description of polymerization processes, ionic activators, and useful scavenging  
3 compounds.

4           Slurry or gas-phase reaction processes can use pre-polymerization of  
5 the supported invention catalyst to further control polymer particle morphology, as  
6 is known in the art. For example, such reaction can be accomplished by pre-  
7 polymerizing a C<sub>2</sub>-C<sub>6</sub>  $\alpha$ -olefin for a limited time. Ethylene contacts the supported  
8 catalyst at between -15° to 30°C and ethylene pressure of up to 250 psig (1724  
9 kPa) for 75 min to obtain a polyethylene coating on the support (30,000-150,000  
10 molecular weight). The above polymerization process can then use the pre-  
11 polymerized catalyst. Additionally, polymeric resins may be used as a support  
12 coating, typically by suspending a support in dissolved polystyrene resin or similar  
13 material followed by separation and drying.

14           The invention catalyst compositions can be used individually as  
15 described above or can be mixed with other known polymerization catalysts to  
16 prepare polymer blends. Monomer and catalyst selection allows polymer blend  
17 preparation under conditions analogous to those using individual catalysts.  
18 Polymers having increased MWD for improved processing and other traditional  
19 benefits available from polymers made with mixed catalyst systems can thus be  
20 achieved.

## 21 EXAMPLES

22           All batch polymerization reactions were run using the following  
23 procedure. At room temperature, the 0.5 L reactor was charged with 250 ml dry  
24 hexane, 18 ml (14g) 1-octene and 8micro liters TOA (25 wt% in hexane). The  
25 reactor was heated to 140 degrees C and pressurized with ethylene to 265 psi. The  
26 ethylene partial pressure was kept constant during the polymerization by a pressure  
27 regulator. A catalyst solution, preactivated by mixing a one to one molar ratio of  
28 hafnocene to activator in toluene, was pumped into the reactor at a rate to maintain  
29 a small ethylene uptake and keep the temperature at 140-41 degrees C. After 20

1 minutes the ethylene pressure was vented and the reactor contents cooled and  
2 solvents removed to yield the polymer.

3 Example 1

4 This reaction employed diphenyl-  
5 methylene(cyclopentadienyl)(fluorenyl)hafnium dimethyl as the catalyst precursor,  
6 with a dimethylaniliniumtetrakis(pentafluorophenyl)borate activator. The reaction  
7 was run substantially as described above. The average activity for this run was  
8 246 grams polymer/gram catalyst.

9 Example 2

10 This reaction employed dimethylsilanylenyl-bis(indenyl)hafnium di-  
11 methyl as the catalyst precursor and  
12 dimethylaniliniumtetrakis(pentafluorophenyl)borate as the activator. Average  
13 activity was approximately 3200 grams polymer/gram catalyst.

14 Example 3

15 This reaction employed diphenyl-  
16 methylene(cyclopentadienyl)(fluorenyl)hafnium dimethyl as the catalyst precursor  
17 and triphenylmethylmethyl tetrakis(perfluoro)borate as the activator. The average  
18 activity was 1250 grams of polymer/gram catalyst. The reaction was run as  
19 spelled out above.

20 As can be seen by comparing Example 1 (comparative) to Example  
21 3, using triphenylcarbenium cations in the catalyst precursor results in a 3-5-fold  
22 increase in catalyst activity. Similar results were seen when the catalyst precursor  
23 is dimethylsilanylenyl-bis(indenyl)hafnium dimethyl.

1

2 1. A metallocene catalyst system comprising an ion pair formed by contacting  
3 a metallocene and an activator wherein:

4 (a) the metallocene is described by the formula

5  $T(CpR_n)(Cp'R'_m)HfQ_2$  wherein

6 (i) Cp and Cp' are cyclopentadienyl ligands

7 (ii) Each R and R' are the same or different  
8 hydrocarbyl radicals having 1-20 carbon atoms;

9 (iii) T is a bridge between Cp and Cp', and  
10 comprises a substituted or unsubstituted  
11 methylene or silylene radical;

12 (iv) each Q is a hydrocarbyl radical having 1-20  
13 carbon atoms or is a halogen

14 (v) n is the number of hydrocarbyl substituents on  
15 Cp and  $n=0-4$ ;

16 (vi) m is the number of hydrocarbyl substituents on  
17 Cp' and  $m=0-4$ ; and

18 (b) the activator is described by the formula:

19  $[Ar_3C][NCA]$  wherein

20 (i) Ar is an aryl ligand

21 (ii)  $Ar_3C$  is a triarylcarbenium; and

22 (iii) NCA is a non-coordinating anion.

23 1'. The metallocene catalyst system of claim 1 wherein Cp, Cp', R, R', m and n  
24 are selected such that  $CpR_m$  is not equal to  $Cp'R'_n$ .

1

2 2. The catalyst system of claim 1, wherein the non-coordinating anion is  
3  $A(Ph^*)_3X$  wherein

- 4 • A is a Group-13 metalloid;
- 5 •  $Ph^*$  is pentafluorophenylene radical
- 6 • X is alkyl-, alkylsily-, or halide-
- 7 substituted phenyl or unsubstituted
- 8 phenyl.

9 3. The catalyst system of claim 2 wherein A is boron.

10 4. The catalyst system of claim 1 wherein  $R_m$  is selected such that  $CpR_m$  forms  
11 a fluorenyl or indenyl radical.

12 4'. The catalyst system of claim 4 wherein the fluorenyl radical is disubstituted  
13 with t-butyl radicals.

14 5. The catalyst system of claim 4 wherein  $R_n$  is selected such that  $CpR_n$  forms  
15 a substituted or unsubstituted cyclopentadienide radical.

16 6. The catalyst system of claim 1 wherein T is  $CZZ'$  or  $SiZZ'$  wherein Z and  
17  $Z'$  are independently selected from substituted or unsubstituted, alkyl or  
18 aryl moieties.

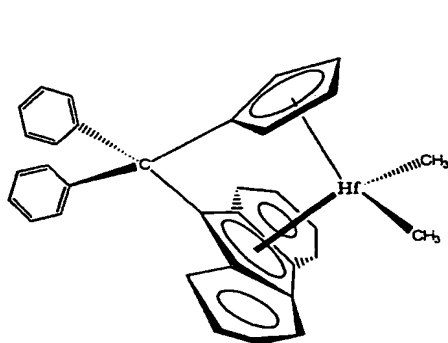
19 6'. The catalyst system of claim 6 wherein Z and  $Z'$  are independently selected  
20 from trialkyl-substituted phenyl moieties.

21 7. The catalyst system of claim 6 wherein Z and  $Z'$  are independently selected  
22 from phenyl and 4-(triethylsilyl)phenyl.

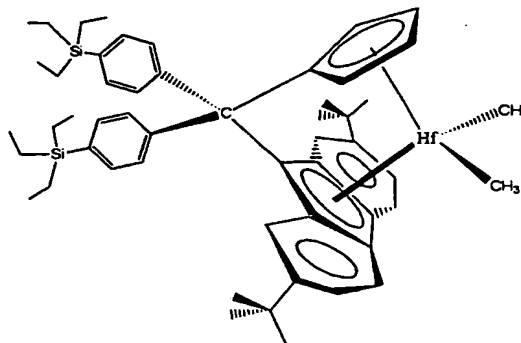
23 8. The catalyst system of claim 7 wherein Z and  $Z'$  is phenyl.

24 9. The catalyst system of claim 7 wherein Z and  $Z'$  are 4-  
25 (triethylsilyl)phenyl.

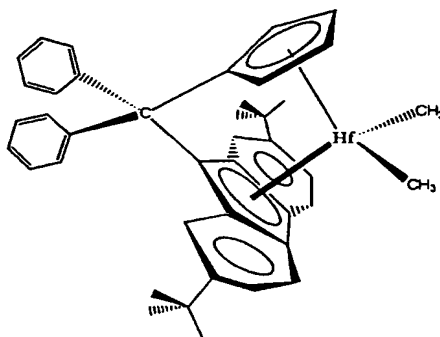
- 1 10. A metallocene catalyst system comprising an ion pair formed by contacting  
2 a metallocene and an activator wherein the metallocene has either formula  
3 I, II, or III and the activator has formula IV:



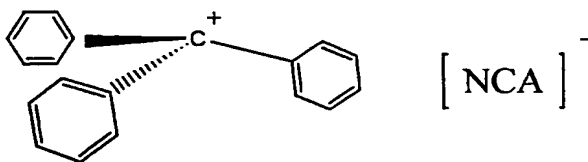
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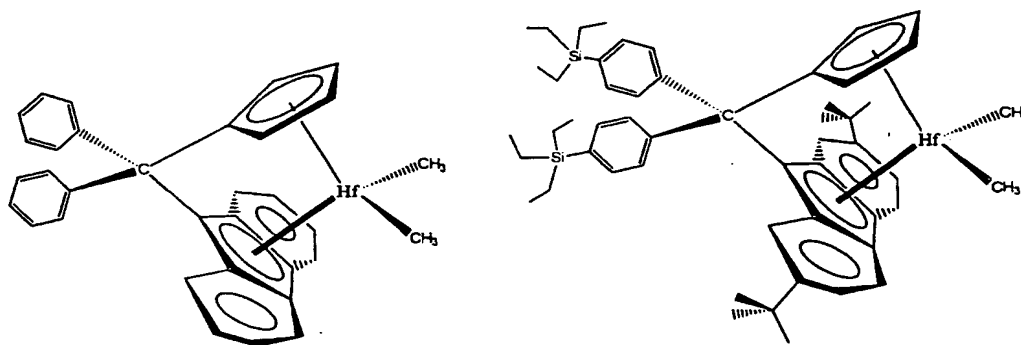
IV.

- 10 11. An olefin polymerization process comprising

- 1 (c) providing a metallocene catalyst precursor described by the  
2 formula  $T(CpR_n)(Cp'R'_m)HfQ_2$  wherein
- 3 (i) Cp and Cp' are cyclopentadienyl ligands
- 4 (ii) Each R and R' are the same or different  
5 hydrocarbyl radicals having 1-20 carbon atoms;
- 6 (iii) T is a bridge between Cp and Cp', and  
7 comprises a substituted or unsubstituted  
8 methylene or silylene radical;
- 9 (iv)
- 10 (v) each Q is a hydrocarbyl radical having 1-20  
11 carbon atoms or is a halogen
- 12 (vi) n is the number of hydrocarbyl substituents on  
13 Cp and  $n=0-4$ ;
- 14 (vii) m is the number of hydrocarbyl substituents on  
15 Cp' and  $m=0-4$ ; and
- 16 (d) providing an activator described by the formula  $[Ar_3C][NCA]$   
17 wherein:
- 18 (i) Ar is an aryl ligand
- 19 (ii)  $Ar_3C$  is a triarylcarbenium; and
- 20 (iii) NCA is a non-coordinating anion;
- 21 (e) forming an active cationic catalyst by contacting the catalyst  
22 precursor with the activator

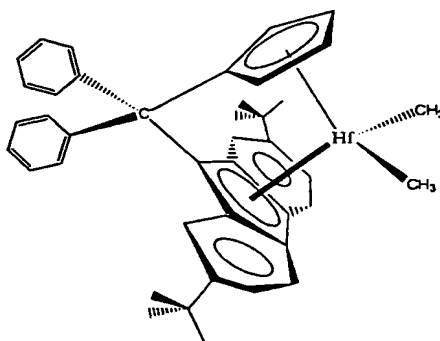
- 1 (f) contacting olefin monomer or olefin monomer mixtures with  
2 the cationic catalyst under olefin-polymerization conditions;  
3 and
- 4 (g) collecting polyolefin.
- 5 11'. The olefin polymerization process of claim 11 wherein Cp, Cp', R, R', m  
6 and n are selected such that  $CpR_m$  is not equal to  $Cp'R'_n$ ; and
- 7
- 8 12. The olefin polymerization process of claim 11' wherein the non-  
9 coordinating anion is  $A(Ph^*)_3X$  wherein
- 10 • A is a Group-13 metalloid;
- 11 •  $Ph^*$  is pentafluorophenylene radical
- 12 • X is alkyl-, alkylsily-, or halide-  
13 substituted phenyl or unsubstituted  
14 phenyl.
- 15 13. The olefin polymerization process of claim 12 wherein A is boron.
- 16 14. The olefin polymerization process of claim 11 wherein  $R_m$  is selected such  
17 that  $CpR_m$  forms a fluorenyl or indenyl radical.
- 18 15. The olefin polymerization process of claim 15 wherein  $R_n$  is selected such  
19 that  $CpR_n$  forms a substituted or unsubstituted cyclopentadienide radical.
- 20 16. The olefin polymerization process of claim 11 wherein T is  $CZZ'$  or  $SiZZ'$   
21 wherein Z and Z' are independently selected from substituted or  
22 unsubstituted, alkyl or aryl moieties.
- 23 17. The olefin polymerization process of claim 16 wherein Z and Z' are  
24 independently selected from phenyl and 4-(triethylsilyl)phenyl.

- 1 18. The olefin polymerization process of claim 17 wherein Z and Z' is phenyl.
- 2 19. The olefin polymerization process of claim 17 wherein Z and Z' are 4-
- 3 (triethylsilanyl)phenyl.
- 4 20. A metallocene catalyst system comprising an ion pair formed by contacting
- 5 a metallocene and an activator wherein the metallocene has either formula I,
- 6 II, or III and the activator has formula IV:

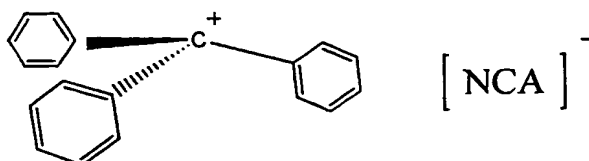


I

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III



1

## IV.

2 21. A metallocene catalyst system comprising an ion pair formed by contacting  
3 diphenyl-methylene(cyclopentadienyl)(fluorenyl)hafnium dimethyl and  
4 triphenylcarbenium tetra(perfluorophenyl)borate.

5 22. A metallocene catalyst system comprising an ion pair formed by contacting  
6 di(4-(triethylsilanyl)phenyl)methylene(cyclopentadienyl)(fluorenyl)hafnium  
7 dimethyl and triphenylcarbenium tetra(perfluorophenyl)borate.

8 23. A metallocene catalyst system comprising an ion pair formed by contacting  
9 diphenylmethylene(cyclopentadienyl)(fluorenyl)hafnium dimethyl and  
10 triphenylcarbenium tetra(perfluorophenyl)borate.

11 24.

12 23. An olefin polymerization process comprising

13 (a) providing a metallocene catalyst precursor described by the  
14 formula  $T(CpR_n)(Cp'R'_m)HfQ_2$  wherein

15 (i) Cp and Cp' are cyclopentadienyl ligands

16 (ii) Each R and R' are the same or different  
17 hydrocarbyl radicals having 1-20 carbon atoms;

18 (iii) T is a bridge between Cp and Cp', and  
19 comprises a substituted or unsubstituted  
20 methylene or silylene radical;

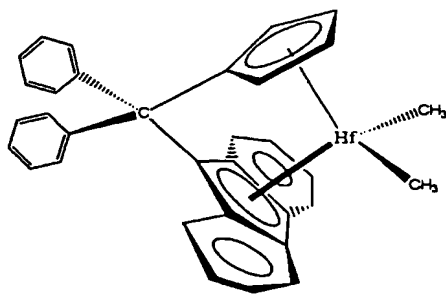
21 (iv)

22 (v) each Q is a hydrocarbyl radical having 1-20  
23 carbon atoms or is a halogen

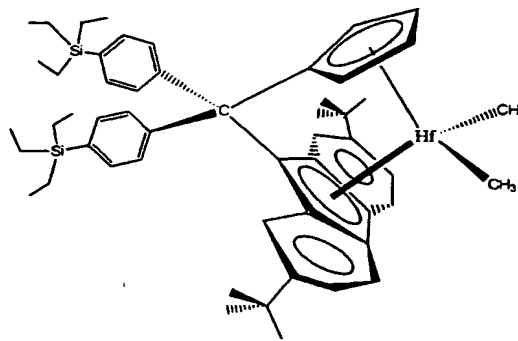
24 (vi) n is the number of hydrocarbyl substituents on  
25 Cp and  $n=0-4$ ;

- 1 (vii) m is the number of hydrocarbyl substituents on  
2 Cp' and m=0-4
- 3 (b) providing an activator described by the formula  $[\text{Ar}_3\text{C}][\text{NCA}]$   
4 wherein:
- 5 (i) Ar is an aryl ligand  
6 (ii)  $\text{Ar}_3\text{C}$  is a triarylcarbenium; and  
7 (iii) NCA is a non-coordinating anion;
- 8 (c) forming an active cationic catalyst by contacting the catalyst  
9 precursor with the activator
- 10 (d) contacting olefin monomer or olefin monomer mixtures with  
11 the cationic catalyst under olefin-polymerization conditions;  
12 and
- 13 (e) collecting polyolefin.
- 14 23'. The olefin polymerization process of claim 23 wherein Cp, Cp', R, R', m  
15 and n are selected such that  $\text{CpR}_m$  is not equal to  $\text{Cp'R}'_n$ ; and
- 16
- 17 24. The olefin polymerization process of claim 23', wherein the non-  
18 coordinating anion is  $\text{A}(\text{Ph}^*)_3\text{X}$  wherein
- 19 • A is a Group-13 metalloid;  
20 •  $\text{Ph}^*$  is pentafluorophenylene radical  
21 • X is alkyl-, alkylsily-, or halide-  
22 substituted phenyl or unsubstituted  
23 phenyl.

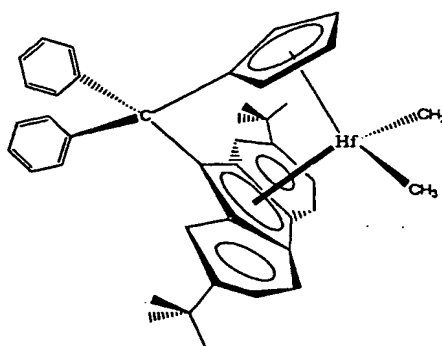
- 1 25. The olefin polymerization process of claim 24 wherein A is boron.
- 2 26. The olefin polymerization process of claim 23 wherein  $R_m$  is selected such  
3 that  $CpR_m$  forms a fluorenyl or indenyl radical.
- 4 27. The olefin polymerization process of claim 26 wherein  $R_n$  is selected such  
5 that  $CpR_n$  forms a substituted or unsubstituted cyclopentadienide anion.
- 6 28. The olefin polymerization process of claim 23 wherein T is CZZ' or SiZZ'  
7 wherein Z and Z' are independently selected from substituted or  
8 unsubstituted, alkyl or aryl moieties.
- 9 29. The olefin polymerization process of claim 28 wherein Z and Z' are  
10 independently selected from phenyl and 4-(triethylsilyl)phenyl.
- 11 30. The olefin polymerization process of claim 29 wherein Z and Z' is phenyl.
- 12 31. The olefin polymerization process of claim 29 wherein Z and Z' are 4-  
13 (triethylsilyl)phenyl.
- 14 32. A metallocene catalyst system comprising an ion pair formed by contacting  
15 a metallocene and an activator wherein the metallocene has either formula  
16 I, II, or III and the activator has formula IV:



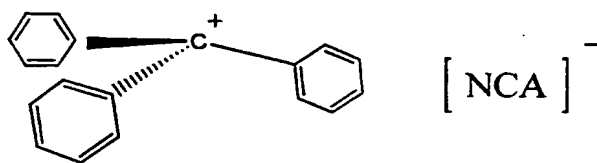
I



II



III



IV.

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 00/29197

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 7 C08F10/00 C08F4/645

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, CHEM ABS Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 708 117 A (SUMITOMO CHEMICAL CO) 24 April 1996 (1996-04-24)  page 5, line 54 -page 6, line 10; examples 7,8	1-18,20, 21, 23-30,32
X	WO 97 22635 A (EXXON CHEMICAL PATENTS INC) 26 June 1997 (1997-06-26) cited in the application	1-6, 11-16, 23-28
A	page 7, line 26 -page 8, line 4; examples 1.18,1.20,2.1; tables 1,2	7-10, 17-22, 29-32
X	US 5 767 208 A (CROWTHER DONNA JEAN ET AL) 16 June 1998 (1998-06-16) cited in the application tables 1,2	1-6, 11-16, 23-28
	-/--	

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

## \* Special categories of cited documents:

\*A\* document defining the general state of the art which is not considered to be of particular relevance

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\*O\* document referring to an oral disclosure, use, exhibition or other means

\*P\* document published prior to the international filing date but later than the priority date claimed

\*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

\*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

\*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

\*Z\* document member of the same patent family

Date of the actual completion of the international search

5 February 2001

Date of mailing of the international search report

02/03/2001

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# INTERNATIONAL SEARCH REPORT

Inter. Jnal Application No

PCT/US 00/29197

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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X	DATABASE CHEMABS 'Online! CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; MATSUKAWA, TETSUYA ET AL: "Manufacture of stereospecific vinyl chloride-based polymers" retrieved from STN Database accession no. 125:276902 XP002159429 abstract & JP 08 208736 A (CHISSO CORP, JAPAN) 13 August 1996 (1996-08-13) -----	1-3

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